

## **Pair distribution function studies of gold nanoparticle ensembles: the challenge and importance of moving beyond ensemble averaged structural descriptions**

The catalytic activity of gold stems predominantly from the presence of under-coordinated atoms at nanoparticle surfaces. A challenge of great importance is thus the quantitative structural description of atomic positions in ensembles of nanoparticles, in particular, determination of the bond distances of atoms at or proximal to nanoparticle surfaces. While this information is contained within the experimentally determined pair distribution function (PDF), there are complications that must be overcome in the construction and refinement of models that account for surface relaxation effects. These challenges are discussed with respect to PDF studies of small gold nanoparticles, where there are comparable numbers of atoms near or at the surface and in the particle interior, particularly for particles smaller than  $\sim 2$  nm. In the light of some recent catalytic studies described in the literature, we discuss how ensemble averaged structural models may impair an understanding of structure-property relations in nanoscale catalysts.